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The Scattering by Two-Angle Ratio (STAR) light scattering method described in this article is based on a new analysis of a well-established theory in the literature that describes black carbon soot as fractal agglomerates. Previous analyses have shown that the measured scattering signals at two appropriate angles can be used to determine the mean agglomerate particle size and mass concentration. The current work shows that a dimensionless invariant function of the two-angle scattering ratio can be defined ($C_m$#), for computation of the mass concentration and mean agglomerate size. In addition, the three soot optical properties can be combined into one overall soot property constant, $S_p$, which, based on literature measurements of each component property, is also near invariant for a variety of fuel and combustor conditions. Research literature on optical parameters has been used (without resorting to arbitrary calibrations) to compute values of the gas phase soot mass concentration. In a companion article (Holve et al. 2011), measurements of diesel and gas turbine engines show that the model for interpreting scattering measurements from STAR is in reasonable agreement with gravimetric measurements.

1. INTRODUCTION

Long sample times are virtually impractical for measurements of gas turbine engines and many users have an interest in finding a fast and accurate substitute measurement technique for the conventional mass sampling EPA Method 5. A variety of techniques, including optical absorption, ultrasonic, tribocharging, and others, have been tried, but up to now, all have suffered from various limitations, including lack of robustness, accuracy, size information, cost, etc. The ideal requirement is that an advanced in situ sensor obtains both particle size distributions and concentrations in a relatively short period of time and the instrument provides a direct or correlated mass concentration measurement. The device should also be simple to operate, portable, and robust for operation under high-temperature field conditions. An instrument has been designed, fabricated, and tested (designated as STAR, Scattering by Two-Angle Ratio) that achieves these objectives and can be used for both gas turbine and diesel engine exhaust soot measurements at concentrations ranging from 1 µg/m³ to values exceeding 1 g/m³ (Holve et al. 2011).

In this article, a theory is outlined, based on Rayleigh-Debye-Gans (RDG) scattering and particle fractal aggregate (PFA) theories for soot agglomerates. The result of this analysis is a simple relationship that gives the particle mass concentration and mean particle size as a function of the measured scattering signals at two different scattering angles relative to the forward direction of a collimated laser beam.

2. DEVELOPMENT OF THEORY FOR STAR

The basic theory using PFA and RDG scattering has been developed previously by numerous authors, and the fundamentals have been summarized in a review paper (Sorensen 2001). In another article (De luliis et al. 1998), the basic two-angle ratio method has been described and experimental measurements show consistent results. However, the analyses used provide implicit solutions so that it is less clear as to the connection among all measurement parameters. In the analysis described below, an explicit formulation is developed for the mass concentration and mean particle sizes, which are directly related to soot optical and physical properties, instrument parameters, and a near-invariant function (defined as the dimensionless $C_m$# for a limited range of fractal dimension, $D_f$, and soot size distributions) that is dependent only on the measured scattering at two angles. Another advantage of this approach is that the soot properties can be combined into one product function, which appears to be near invariant itself.
2.1. Primary Particles and Fractal Soot Agglomerates

Primary particles, with uniform and reasonably well-defined diameter \(d_p\) and density \(\rho_p\), are the building blocks of soot agglomerates. The mass of a primary particle is given by

\[
m_p(g) = \frac{\pi}{6} \rho_p d_p^3 \quad \text{and} \quad A_p = \pi d_p^2,
\]

where \(A_p\) is the external surface area of primary particles, in which contact area is negligible.

It is known that \(d_p\) is approximately constant (25–35 nm) for a wide range of combustion conditions, including a variety of flames, engines, and fuels (Hull et al. 2004; Neer and Koylu 2006).

Fractal aggregates are assembled from primary particles using PFA theory. The number \(n\) of primary particles in a fractal aggregate of diameter \(d_g = 2R_g\) (based on radius of gyration, \(R_g\)) is given by

\[
n = k_n(d_g/d_p)^{D_f},
\]

where \(D_f\) is the fractal dimension, measured in a variety of flames and engines (Sorensen 2001). The radius of gyration is the natural optical size descriptor of soot agglomerates and is used to characterize the optical structure function. The gyration diameter can be measured experimentally by using transmission electron microscopy (TEM). However, most submicron particle distribution measurements are now based on the mobility diameter, \(d_m\), obtained by using mobility sizing instruments. The relationship between \(d_g\) and \(d_m\) will be discussed in further detail below.

There is general agreement (Sorensen 2001) that the fractal dimension is in the range of 1.7–1.9, and a mean value of \(D_f = 1.8\) is used. A question remains as to the appropriate value of \(k_n\), given that literature values range over a factor of 2, from \(k_n = 1.3\) (Sorensen and Roberts 1997) to \(k_n = 1.7–2.6\) determined by TEM measurements of diesel soot gyration diameters and light scattering measurements (Koylu et al. 1995; Hu et al. 2003; Hu and Koylu 2004). All sets of results appear to be internally consistent, but this range of uncertainty is large, given the better than 5% precision of optical measurements.

The analysis below was initially developed assuming that \(k_n\) requires experimental determination and thus discrimination of the “correct” fundamental value. Other literature results based on the direct measurement of particle mass as a function of mobility diameter were evaluated (Park et al. 2003a; Słowiński et al. 2004), and these independent results show excellent agreement in their measurements obtained from different combustion systems (propane/air, and a diesel engine) for fuel/air equivalence ratios below 2 and mobility diameters \(>100\) nm. From this data, the fractal dimension is \(D_f = 1.79\), and \(k_n \approx 2.06\% \pm 15\%\), consistent with the results of Hu and Koylu.

2.2. Scattering Theory for Soot Agglomerates

Initially, two methods were used to compute the scattering from particles larger than the primary particle diameter. The first is based on RDG theory (Sorensen 2001), which has an extensive literature. The second theory is the one developed by Hull et al. (2004). Using a coupled dipole scattering model, Hull shows that the refractive index of a soot agglomerate is linearly proportional to the agglomerate density for spherical fill ratios \(>15\%\), corresponding to \(d_g < 300\) nm. The Maxwell-Garnett theory (Sorensen 2001) also shows the same result for one material uniformly diluted within another; in this case carbon primary particles embedded in an equivalent porous sphere. Although aggregates are not generally uniform, this approximation appears to be valid for the range described earlier.

Using the results mentioned above for \(k_n\) and \(D_f\), combined with Equation (1), the agglomerate density can be calculated and compared with the measured density results of Park et al. (2003b), showing good agreement. Using the spherical fill model of Hull et al. (2004), the nondimensional scattering cross-section \(F(d_g, m(d_g))\) can be calculated using the Mie theory for spherical particles as a function of soot agglomerate diameter and variable refractive index, \(m(d_g)\), which is also a function of the agglomerate diameter.

Comparison of results shows that RDG and the spherical fill model of Hull et al. (2004) agree to better than 10% for soot mobility diameters up to 300 nm at 90 and 30° scattering angles. Above this diameter, the spherical fill model (below 10% fill) does not accurately characterize ramified agglomerate particles according to Hull et al. Sorensen (2001) shows that for soot particles or any ramified particle with fractal dimension less than 2, the phase shift parameter \(\rho = 2\pi d_p m(\lambda - 1)\) is less than unity, where \(m(\lambda - 1)\) is the effective agglomerate refractive index. Sorensen also shows that RDG is accurate within 10% of detailed numerical computations for the fractal dimension \(D_f = 1.8\) and \(\rho < 1.0\).

As confirmed by measurements (Holve et al. 2011), gas turbine and small diesel engine soots tend to be smaller than 350 nm, so that either Mie or RDG will provide reasonably accurate results. As developed below, RDG gives an explicit sensitivity analysis to uncertainties in the primary particle physical and optical properties. The utility of using the Mie theory has been to provide an independent verification of the RDG calculations.

2.2.1. RDG Scattering Theory for Monodisperse Soot

The basis of RDG scattering is the superposition of primary particle scattering. The dimensional scattering cross section for light collection in the plane perpendicular to the polarized light vector is \(\sigma(d_p, m, \Omega, \theta)\) (cm\(^4\)) for a primary particle in the Rayleigh range \((d_p \ll \lambda)\) and is given by (Van de Hulst 1981)

\[
\sigma(d_p, m, \Omega, \theta) = \left(\frac{2\pi}{\lambda}\right)^4 \left(\frac{d_p}{2}\right)^6 f(m) \Omega,
\]
where $d_p$ (cm) is the primary particle diameter, $\Omega$ (sr) is the receiver lens solid angle aperture for scattered light, $m$ is the complex refractive index of a primary particle, $\lambda$ (cm) is the illumination wavelength, and the scattering refractive index function is

$$f(m) = \frac{(m^2 - 1)^2}{(m^2 + 2)}. \quad [3]$$

The integrated scattering cross section of an agglomerate of gyration diameter $d_g$ for a receiver lens aperture $\Omega$ (sr) is related to the primary particle scattering cross section at angle $\theta$ by

$$\sigma(d_g, m, \Omega, \theta) = n^2 \sigma(d_p, m, \Omega) S(qd_g), \quad [4]$$

where

$\sigma(d_g, m, \Omega, \theta)$ (cm$^2$) is the scattering cross section of a single agglomerate particle,

$n$ is the number of primary particles, $d_p$, in the agglomerate,

$\sigma(d_p, m, \Omega)$ (cm$^2$) is the scattering cross section of a single primary particle,

$S(qd_g)$ is the structure factor characterizing agglomerate density and angular scattering distribution,

$q = (4\pi\lambda_0\sin(\theta/2))$ is the scattering wave vector at scattering angle, $\theta$, and

$\theta$ is the mean scattering angle for receiver lens.

The standard formulation for PFA (Equation (1)) is used to describe the fractal relationship of $n$ to the agglomerate size, based on the radius of gyration, $d_g$, and primary particle size, $d_p$.

The total scattered power into a detector depends on the integration of the illumination intensity for all particles in the Gaussian beam sample volume. Integration over the intensity distribution shows that the average area intensity in the sample volume is simply the total laser power, $P_l$ (watts), divided by the beam area as defined by the $1/e^2$ beam diameter, $W_o$, or

$$I_{\text{avg}} = 4P_l/\pi W_o^2. \quad [5]$$

This assumes that the beam diameter is constant over the length of the sample volume. The total scattered light at a given angle, $P_T$ (watts), from a monodisperse population number density, $N_t$, of agglomerates in the sample volume is then simply

$$P_T = I_{\text{avg}} N_t \sigma(d_g, m, \Omega, \theta), \quad [6]$$

where

$V_s$ (cm$^3$) = $\pi W^2_o l/4$ is the particle scattering sample volume,

$W_o$ (cm) = $1/e^2$ is the beam waist diameter of illuminating laser beam,

$l$ (cm) is the length of sample volume defined by detector slit width, and

$N_t$ (cm$^{-3}$) is the average total number of agglomerate particles per unit volume.

The next step is to develop a second relationship that specifies the total mass concentration of a monodispersion of agglomerates of size $n$ (related to $d_p$ and $d_g$) as follows:

$$C_m = N_t m, \quad [7]$$

where $m = nm_p$ and $m_p = (\pi/6)\rho_p d_p^3$.

Ratios of Equations (7) and (6),

$$\frac{C}{P_T} = \frac{N_t n m_p}{I_{\text{avg}} V_s N_t \sigma(d_g, m, \Omega, \theta)} \quad [8]$$

Up to this point, the derivation follows that of most previous researchers (Sorensen 2001).

Substituting Equations (4)–(7) into Equation (8) and rearranging give the first equality in Equation (9). The second equality is obtained by separating primary soot properties, instrument properties, and agglomerate structure, defining a new function (the $C_m#$) shown to be dependent only on the agglomerate gyration and primary particle diameters.

$$\frac{C_m}{P_T} = \frac{m_p}{P_l \sigma(d_p, m, \Omega)nS(qd_g)} = \left(\frac{\rho_p}{(d_p/\lambda)^3-Df f(m)}\right) \times \left(\frac{\lambda}{P_l / \Omega}\right) C_m#(qd_g). \quad [9]$$

The first bracketed term $S_p \equiv \{\rho_p/[(d_p/\lambda)^3-Df f(m)]\}$ is a function only of the soot properties (where $d_p$ is normalized by the laser wavelength) and is proposed to be nearly invariant as discussed further below. The second bracketed term $[\lambda/(P_l / \Omega)]$ is a function only of the instrument configuration. The $C_m#$ is defined as

$$C_m# \equiv \frac{(\lambda / \sigma)}{(\mu c)} \frac{d_f}{n S(qd_g)} \quad [10]$$

For known and near constant values of $D_f$, it can be shown that the $C_m#$ is a dimensionless (near) invariant function only of the measured scattering ratio $R_{02/01}$ at two defined detector angles.

A second expression from Equations (4) and (6) is derived for the ratio of scattering at two suitable angles:

$$R_{02/01} = \frac{P_{T2}}{P_{T1}} = \frac{S(q_{02}d_g)}{S(q_{01}d_g)}. \quad [11]$$

Equation (11) defines a unique expression for $d_g$ in terms of the measured scattering ratio, $R_{02/01}$. Again, $D_f$ is assumed to be near constant for typical engine operating conditions.
De luliis et al. (1998) and others have used the structure function recommended by Lin et al. (1989), expressed in terms of the radius of gyration as
\[ S(q R_g) = \left\{ 1 + (8/(3 D_f)) (q R_g)^2 + 2.5(q R_g)^4 - 1.52(q R_g)^6 + 1.02(q R_g)^8 \right\}^{-D_f/8}. \] \[ 12 \]

This function has been compared with more precise forms based on the density autocorrelation of a fractal aggregate, which does not have a hard sphere boundary. The choice of the density autocorrelation function roll-off (Gaussian) is itself based on best fit with experimental data, but Equation (12) is within 10% of the values used by a variety of researchers (Sorensen 2001).

2.2.2. Explicit Solution for \( nS(q_d) \)

Although the results of Lin et al. (1989) for \( S(q R_g) \), combined with the empirical expressions for \( n \), (Equation (1)) can be used as in the past, a more fundamental approach that eliminates \( k_o \), as an independent parameter has been found. Nicolai et al. (1994), following the work of Teixeira (1986), provide an explicit formulation that results in an exact solution for the product \( nS(q) \), where in their notation, \( S(q) \) implies \( S(q_d) \). As further explained below, the formulation by Nicolai et al. provides a more general relationship for \( k_o \) and \( S(q) \) that is consistent with the empirical expression given in Equation (12). In their analysis, the total number of monomers in a monodisperse aggregate is
\[ n = a(d_p/2)^{D_f}. \] \[ 13 \]

Equation (13) is equivalent to Equation (1). Therefore,
\[ k_o = a(d_p/2)^{D_f}. \] \[ 14 \]

As noted by Nicolai et al. (1994) in the limit of large \( d_p \), there is an exact solution for \( a \), which is based on the definition of the radius of gyration and particle mass. These quantities, in turn, are based on the average pair correlation function of monomers within an aggregate particle given by
\[ g(r) = \left[ \frac{D_f}{(4\pi d_p/2)^{D_f}} \right] [(r)^{D_f-3}] f(r/\xi). \] \[ 15 \]

Nicolai et al. (1994) state that \( d_p^* \) depends on the local aggregate structure and is of the order of the monomer size, and they assume that it is equal to the measured monomer size. For soot aggregates, there is monomer overlap (Brasil et al. 2000) and therefore \( d_p^* = d_p \) is not necessarily true. Thus, \( d_p^* \) as a scaling length for a given agglomerate structure must be measured or inferred. Equation (15) is based on the fundamental concept of a fractal, where the number of primary particles at a given radius for a pure fractal is given by \( n_r = \{r(d_p/2)^{D_f} \} \). In Nicolai et al. and Teixeira (1986), this condition is used to explicitly define the constant \( D_f/4\pi \), based on the local particle density for a spherical volume.

The quantity \( f(r/\xi) \) is a cutoff function to account for the finite size of the fractal agglomerate. This function is not known exactly but is assumed to take the form of a “stretched” exponential, which has the characteristic that it is close to unity for \( r/\xi < 1 \), and decreases faster than any power law for \( r/\xi > 1 \), i.e.,
\[ f(r/\xi) = \exp[-(r/\xi)^\gamma]. \] \[ 16 \]

The stretched exponential is an appended function that accounts for the finite dimension of an agglomerate, which deviates from a pure fractal for values of \( r > d_p/2 \). For large values of \( \gamma \) approaching infinity, \( g(r) \) approaches a pure fractal (\( n_r = \{r(d_p/2)^{D_f} \} \) for all \( r < \xi \) and \( n_r = 0 \) for \( r > \xi \)). For smaller values of \( \gamma \), \( g(r) \) deviates from a pure fractal, based on the cutoff function and \( \gamma \), that in part determines \( k_o \), and thus the number of primary particles in an agglomerate of diameter \( d_p \).

Using these relationships in the limit of large \( d_p \), Nicolai et al. derive the solution for \( a \) as
\[ a = \left\{ \frac{2\Gamma(D_f/\gamma)}{\Gamma(D_f+2)/\gamma} \right\}^{D_f/2} \times \left( \frac{D_f}{(d_p/2)^{D_f}} \right). \] \[ 17 \]

Thus, combining Equations (13) and (14) results in
\[ k_o = \left\{ \frac{2\Gamma(D_f/\gamma)}{\Gamma(D_f+2)/\gamma} \right\}^{D_f/2} \times \left( \frac{D_f}{(d_p/2)^{D_f}} \right) \times \left( \frac{d_p}{d_p^*} \right)^{D_f}. \] \[ 18 \]

This result shows that \( k_o \) is dependent on the fractal dimension, \( D_f \), the sharpness of the cutoff function, \( \gamma \), and the ratio \( d_p/d_p^* \).

From the second mass balance equation, Nicolai et al. determine the relationship for the agglomerate scaling length \( \xi \) from
\[ R_g^2 = \frac{\xi^2\Gamma([D_f+2]/\gamma)}{2\Gamma(D_f/\gamma)}. \] \[ 19 \]

For typical values of \( D_f \) and \( \gamma \), \( \xi \approx 1.4 R_g \), i.e., the scaling length \( \xi \) is larger than the radius of gyration, \( R_g \).

Calculation of \( k_o \) as a function of \( \gamma \), with \( D_f \) as a parameter [for \( (d_p/d_p^*)^{D_f} = 1 \)], gives the results shown in Figure 1. From this figure, \( k_o \) has a weak dependence on \( D_f \), which are all identical for a Gaussian distribution with \( \gamma \) equal to 2. Although it appears that another unknown \( \gamma \) has been merely substituted for \( k_o \), it will be shown below that the product \( nS(q) \) is dependent only on the ratio \( d_p/d_p^* \).

From Equations (9) and (10), it is the product \( nS(q) \) that is important for computing the mass concentration. Following
FIG. 1. Variation of $k_0$ as a function of $\gamma$, with $D_f$ as a parameter, computed from Equation (18).

Nicolai et al. (1994), this product for general conditions is given by

$$nS(q) = 1 + D_f / (d_p^*/2)^{D_f} \times \int_{d_p^*/2}^{\infty} r^{D_f-1} \exp(-[r/\xi]^\gamma) \times \sin(q r)/q r \, dr.$$ \hspace{1cm} \text{[20]}

Making the change of variable $x = 2r/d_p^*$, Equation (24) becomes

$$nS(q) = 1 + D_f \int_1^{\infty} x^{D_f-1} \exp\left(-\left[x d_p^*/2 \xi\right]^\gamma\right) \times \left[2 \sin(q d_p^*/2)/q d_p^*\right] x \, dx.$$ \hspace{1cm} \text{[21]}

Note that in Equation (21), there is no explicit definition of $k_0$. The only parameters are $q$, $d_p^*$, $D_f$, and $\gamma$. In the limit of $qd_p^* \gg 1$,

$$nS(q) = \left[D_f \Gamma(D_f - 1) \sin((\pi/2)(D_f - 1))\right] \left[(q d_p^*/2 - D_f)^{-D_f}\right]$$

\hspace{1cm} \text{[22]}

or substituting for $q = (4\pi/\lambda)\sin(\theta/2)$ and transposing terms $(d_p^*/\lambda)^{D_f} nS(q) = \{2\}/(2\pi \sin(\theta/2))^{D_f}$, where the quantity in $\{\}$ is $2.0 \pm 2\%$ for $D_f = 1.6 – 2.0$. This result shows that the $C_m#$ (Equation (10)) is dependent only on the fractal dimension for a defined light scattering geometry, $\theta$, and the ratio $(d_p^*/d_p)$, i.e., the mass concentration measurement, is independent of the overall agglomerate structure.

Using Equation (19) to define $\xi$ in terms of $2R_g = d_p$, one can numerically integrate Equation (21) to obtain a unique function dependent only on $d_p$ for specified values of $\theta$ and $D_f$. The calculated product $nS(q)$ (related to the inverse $C_m#$) is illustrated in Figure 2. The important result here is that similar to the large agglomerate results (Equation (22)), $nS(q)$ (and the $C_m#$) varies less than $\pm 9\%$ for values of the cutoff function parameter, $\gamma$, ranging from 1.6 to 2.5, with a mean value of $\gamma = 2$ used for most current analyses, and $k_0$ does not appear explicitly, but rather is embedded as a function of $D_f$, $\gamma$, and $d_p^*/d_p$. This is in contrast to Figure 1, where $k_0$ varies $\pm 21\%$ for $\gamma$ ranging from 1.6 to 2.5. Also shown in Figure 2 is a comparison of the commonly used empirical curve fit function for $S(q)$ of Lin et al. (1990) based on $\gamma = 2$, and the calculated value of $k_0 = 2$ from Figure 1, assuming $d_p^*/d_p = 1$. The two results are in good agreement. In addition, this figure shows the variation for $\gamma = 2$, with $D_f$ varying from 1.7 to 1.9, giving a $C_m#$ variation of less than $\pm 15\%$ for the range of measured soot fractal dimensions.

It is concluded that the product $nS(q)$ is only weakly dependent on assumptions of the detailed cutoff function, whereas $n$ and $S(q)$ independently have significantly greater variation. For mass concentration measurements, this shows that the product $nS(q)$ is a more fundamental and invariant expression for the structural scattering effects of a soot agglomerate.

For a defined instrument geometry, $\theta$, the $C_m#$($q$) is a unique and invariant function of $d_p$ for known $D_f$. The equations and results of Nicolai et al. (1994) and Teixeira (1986) are in agreement with Monte Carlo (MC) results of Sorensen (2001), Lin et al. (1989), and Lattuada et al. (2003), except for the density correlation function constant used in the agglomerate mass balance, which in the Nicolai formulation is characterized by $d_p^*/d_p$. From Nicolai, the structure function constant and scaling radius $(C = 1, 2\xi/d_p \approx 1.55$ for $\gamma = 2$) agree with MC results. Useful results
that arise from the Lattuada MC simulation are their finding values for $\gamma = 2.2$ and $2\xi/d_\theta \approx 1.65$, in reasonable agreement with Nicolai. The numerical MC results described earlier, using point contact assumptions to define agglomerate formation, give $k_0$ in the range of 1.2–1.4 (Sorensen 2001). The difference of MC results with experimental soot measurements of $k_0$ has been discussed by Oh and Sorensen (1997) and Brasil et al. (2000), and has been attributed to particle overlap, possibly due to sintering at high temperatures following agglomerate formation. In both these MC models, values of $k_0 \approx 2$ can be generated based on monomer overlap of approximately 25%. In both articles, the authors have stopped short of a definitive conclusion, given that there are no quantitative overlap measurements for soot.

Both MC and Nicolai models can account for higher values of soot $k_0$, through monomer overlap and $d_p^\alpha$ scaling, but at present, there are no independent measurements of these parameters. Thus, $k_0$ for soot must be ultimately determined experimentally, particularly because soot agglomerates endure sintering and condensation phases following formation. For $\gamma \approx 2$ and $D_p = 1.8$, the measurement of $k_0 \approx 2$ for soot effectively defines $d_p^\alpha/d_p \approx 1$ in the Nicolai model (Figure 1), where $d_p^\alpha$ accounts for the effective soot monomer packing density (Sorensen, personal communication, January 2011). If there is particle overlap, then the effective volume of the monomers used in Equation (2) will also change. For sphere overlap of 25%, calculations show that the monomer volume change is small, less than 6%.

The formulae above are based on a monodisperse agglomerate. Similar results will be derived for the polydisperse case below, where the mass mean diameter is used to define $d_{go}$ and $n_o$, and a moment function ratio is based on the typical agglomerate distribution width. Although Nicolai et al. have developed a theoretical expression for the monodisperse $nS(q)$, for the practical polydisperse case, they have developed individual moment functions for $n$ and $R_g (=d/2)$. In the following, the Nicolai et al. formulation for polydisperse size distributions has been modified using the moment functions for the product $\{nS(q)\}$.

### 2.2.3. Scattering of Polydisperse Soot

For polydisperse soot, a similar derivation as described above is followed, except for the general polydisperse case, one sums the contributions from each agglomerate particle size class of the distribution for the total mass and total scattering. Thus, the total scattering cross section, $\sigma_d$, of the polydisperse agglomerate distribution is given (from Equation (4)) by

$$\sigma_d = \Sigma \Delta N_i \sigma(d_{gi}, m, \Omega, \theta) = \Sigma \Delta N_i n_i^2 \sigma(d_p, m, \Omega, \theta) S(qd_{go}).$$  \[23\]

where $\Delta N_i$ is the number of agglomerate particles in the sub-class $i$ and the sum, $\Sigma$, is taken over the entire size range. Both lognormal and scaling function distributions have similar distribution shapes, with lognormal giving a longer tail. For the polydisperse calculations in the following, scaling function distributions (Sorensen 2001), which evolve in a self-preserving fashion with time, were used to describe soot agglomerates. For sufficiently long aggregation periods, the aggregate size distribution has the form, independent of time, $p(x_i) = A x_i^{-\tau} \exp(-\alpha x_i)$, where $x_i = n_i/n_o$, $n_i$ is the number of monomers in a cluster aggregate $i$, $n_o$ is the mean cluster size of the distribution, $\tau$ is the scaling parameter, $\alpha = 1 - \tau$, and $A$ is equal to $\alpha^{2-\tau}/\Gamma(2-\tau)$. Sorensen (2001) recommends $\tau = 0.24 \pm 0.23$ (which characterizes the distribution width) for diffusion-limited colloid aggregation (DLCA). The following calculations have used $\tau = 0.0$ for the results in Figures 3 and 4. Comparison calculations at $\tau = 0.25$ and 0.5 show less than 5% variation for the $C_m^\#$, and approximately ±10% for $d_p$ at $\tau = 0.25 \pm 0.25$. The reason for this low sensitivity to the distribution width, $\tau$, is that moments are taken around the product $nS(q)$ for the $C_m^\#$.

Following the monodisperse derivation, (Equation (7)), the total mass concentration of the distribution is given by

$$C_m = \Sigma \Delta N_i n_i m_p.$$  \[24\]

Each of these equations can be normalized by the mean values of the distribution parameters, $d_{go}$, $n_{go}$, and the total number of particles in the distribution, $N_i$. Thus,

$$\sigma_d = N_i n_{go}^2 S(qd_{go}) \sum \Delta N_i n_i^2 \sigma(d_p, m, \Omega, \theta) S(qd_{go})$$  \[25\]
The subscript “o” refers to the scattering mean value of gyration diameter determined by the scattering ratio measurement, which for an agglomerate polydispersion gives an implicit expression for $d_{go}$ as a function of $R_{θ/θ1}$:

$$R_{θ/θ1} = \left( \frac{M_{2θ2}}{M_{2θ1}} \right) \left( \frac{S(qθd_{go})}{S(qθd_{go})} \right).$$  \[30\]

Similarly, the relationship for the mass concentration $C_m$ is

$$C_m = \left( \frac{ρ_p}{(d_p/λ)^{Df}} \right) \left( \frac{(λ/ρ_p)}{P_1Ω} \right) M_{2θ1}^#(qd_{go}).$$  \[31\]

The first soot property term is in units of concentration (g/m³), and the instrument property (second parenthesis) is the nondimensional scattering signal. Equations (30) and (31) provide a unique solution to the measurement and interpretation of mass soot concentrations. These expressions show a simple, yet fundamental relationship for the mass concentration in terms of $d_{go}$, which is a function only of the measured scattering signals at two detectors.

To solve this problem generally, one only needs to model the polydisperse distribution shape for the aggregates. Experimental measurements, as shown by Koylu et al. (1995) and Sorensen and Feke (1996), confirm that a lognormal size distribution function is appropriate for number, area, and volume distribution characterization. At the same time, scaling distributions based on $n$ are also used, are similar, and can be related to the Rosin-Rammler or Weibull distributions. The author has shown that the ultimate result for computing the $C_m#$ and mean diameter $d_{go}$ is insensitive (< ±10%) for typically measured soot size distributions, including lognormal, Rosin-Rammler, or scaling distributions.

Figure 3 shows values of the $C_m#$ for a range of second detector angles (90–180°), using a reference angle of $θ_1 = 30°$ for the computation of the scattering ratio $R_{θ/θ1}$, fractal dimension $D_f = 1.8$, and typical polydisperse soot distribution parameters. Also shown are data points at 90° for variations of $D_f = 1.7–1.9$, and a range of typical distribution widths as described earlier. A simplified analytical analysis also shows that the assumed distribution width variance for a lognormal distribution (e.g., $σ = 1.6–2.0$) has a minimal influence on the polydisperse $C_m#$.

Given the similarity of the curves for the larger angles, and using the large limit result from Equation (22), one can show that for large angle detectors greater than 90°, all curves collapse (within 5%) to the 180° function, $C_m#$, when the angular-dependent $C_m#$ is normalized by $R_{θ/θ1}$. Also shown is the comparison 180° monodisperse $C_m#$ that converges to the polydisperse values at large and small values of $n_{θ1}$, $M_1M_{2θ1}$ reduce to unity and the polydisperse values of $C_m#$ agree with the monodisperse results. The maximum departure of polydisperse from monodisperse $C_m#$ is approximately 40%. Thus, one
The polynomial fit function of $R_{2001}$ can be used to describe the mass concentration structure factor ($C_m$) for typical polydisperse soot and a general range of optical geometries.

In the large agglomerate limit, where $q d_g > 2.6$ (Figure 3), $M_1/M_2 = 1.0$ for any agglomerate distribution, and the product of $n_o S(q d_{go})$ follows the same form as derived in Equation (22):

$$C_m = \left\{ \frac{(2/3\pi^3)(\lambda/d_p)^D_f}{(n_o S(q d_{go}))} \right\}, \quad \text{[32]}$$

or

$$C_m = \frac{C_m}{[\sin(\theta_2/2)]^{D_f}} = (2\pi)^{D_f}/(3\pi^3),$$

which agrees with the computations of Figure 3 and is independent of the agglomerate diameter. Combining all terms with dependence on $D_f$ from Equation (31) with Equation (32) gives an overall sensitivity of $C_m$ to uncertainty in the fractal dimension ($\pm \Delta D_f \approx 0.1$) as $\Delta C_m/C_m \approx -1.44\Delta D_f \approx 15\%$.

Small particle limit: $C_m = (2/3\pi^3)(\lambda/d_p)^D_f$, where $n_o$ and $S(q d_{go}) = 1$. This result agrees with the straightforward Rayleigh scattering ($d_p/\lambda \ll 1$) calculation for scattering per unit mass concentration of a primary particle, $d_p$. Figure 3 shows that monodisperse results agree with the polydisperse values in both the small and large limits. For the same mass concentration, the ratio of large agglomerate “enhanced” scattering to independent primary particle scattering is $2/[2(2\pi d_p/\lambda\sin(\theta_2/2))]^{D_f}$ for general conditions, given by the ratio of the $C_m$ for the small and large agglomerate limits.

It is noted that for $R < 40\%$, the $C_m$ is essentially constant (large agglomerate limit mentioned earlier) and the computation of the mass concentration, $C_m$, would be dependent only on the scattering signal from the large angle detector. In this case, one can implement a simpler instrument (patent no. 7782459) with a single detector (e.g., 120) and a shorter laser wavelength to measure the mass concentration, $C_m$, although one would forgo the measurement of $d_{go}$. Measurements (Holve et al. 2011) have shown that the volume mean engine soot agglomerate is typically larger than 100 nm. Using the “large particle” criterion above, where $q d_g > 2.6$, this implies that one should choose $q > 26$, if possible. Using a laser wavelength in the ultraviolet to green range, combined with $\theta > 120$ will achieve the required value of $q > 26$.

Figure 4 shows the corresponding gyration diameters for a range of second detector angles (90 – 180), using a reference angle of $30^\circ$, fractal dimension $D_f = 1.8$, and typical polydisperse soot distribution parameters, computed as a function of the $R$ ratio. Also shown are data points at $90^\circ$ for variations of $D_f = 1.7–1.9$, and a range of typical distribution widths (90 var $D_f$). Parallel to the $C_m$, there are minimal effects of parameter assumptions on this invariant function for optical gyration diameter. Again, the large limit scaling factor, $[\sin(\theta/2)]^{D_f}$, nearly collapses all curves (for large angle detectors greater than 90) to the 180 function ($\pm 10\%$ from $\theta_2 = 120$). Also shown is the comparison 180 monodisperse $d_p$, which gives significantly larger sizes for a given scattering ratio. In contrast to the $C_m$, for particle size measurement, the $[\sin(\theta/2)]^{D_f}$ scaling factor is not sufficiently accurate to use one polynomial fit function, which should be computed for each optical geometry.

3. UNCERTAINTY ESTIMATES FOR STAR THEORY

For a specified instrument geometry, the analysis above has shown that the $C_m$ varies only with the fractal dimension, which is well characterized within the range of $D_f = 1.7–1.9$ for agglomerate soot over a wide range of engine operating conditions. Thus, the primary uncertainties in calculating the particle mass concentration, $C_m$, are the soot properties, $f(m)/\rho_p$, and the nondimensionalized primary particle size, $d_p/\lambda$, as characterized by the first bracketed term of Equation (31), or $S_p = \{[\rho_p f(m)]/(d_p/\lambda)^{D_f}\}$. For the broadest application of Equation (31) for the measurement of $C_m$, it is important to show that $S_p$ is near constant, including conditions in which surface condensation of gas phase hydrocarbons is important. Evaluation of $d_e$ is primarily dependent on $D_f$, with no dependence on soot properties.

3.1. Primary Particle Refractive Index and Density

It is proposed that the refractive index effect has less variance when accounting for the variations in primary particle density. The density is well known for pure carbon, with a value of $2 \text{gm/cm}^3$. Measurements by Park et al. (2003b) and Slowik et al. (2004) give values of density $= 1.7–1.8 \text{g/cm}^3$ for soot primary particles. A wide range of refractive index measurements of carbon soots have been obtained and are summarized by Sorensen (2001), showing a >50% variation in the scattering values of $f(m)$, with a mean value of $m = 1.62–0.66i$. Recent measurements of soot refractive index using scattering and absorption by Shaddix and Williams (2007) give significantly higher values of $m = 1.7 – 1i$, while Bond and Bergstrom (2006) recommend a value of $m = 1.95 – 0.79i$ based on matching the measured values of the absorption coefficient, $\sigma_a = 6\pi E(m)/\rho_p \lambda$ (m$^2$/g) (valid for Rayleigh spheres up to 100 nm), where $E(m)$ is the Rayleigh absorption function. Figure 5 shows the computed variation of $\sigma_a$ and $f(m)/\rho_p$ ($\rho_p = 1.7 \text{g/cm}^3$) with $m_2$ as the complex part of the refractive index for the real refractive index $m_1 = 1.8$. It is interesting to note that $f(m)/\rho_p$ is relatively insensitive to variations in $m_1$, while the absorption coefficient increases significantly with decreasing $m_1$. The graph suggests that a mean value of $m = 1.8 – 0.9i$ is within experimental agreement, and feasible values of $f(m)/\rho_p$ range from 0.22 to 0.27 ($\pm 10\%$ from the mean value of 0.245), considerably higher than those based on previous measurements of $m$. Experimental measurements by Holve et al. (2011) confirm that these self-consistent higher values of $f(m)/\rho_p$ give good agreement with
gravimetric measurements obtained for both gas turbines and diesel engines.

3.2. Size Uniformity of Primary Particles

A variety of measurements on engines and research flames show limited variation (20–40 nm) in the primary particle size for near stoichiometric conditions, which are used for most industrial engines. Specifically, Kazakov and Frenklach (1998) have modeled the condensation/aggregation of soot particles. Their results show that the primary particles quickly (≈30 ms) reach a constant size, followed by aggregation, where the primary particles show less than 14% growth once aggregation begins. It is also known that the primary particle size distribution is relatively narrow, with a lognormal standard deviation, $\sigma \sim 1.2$ (Wang and Sorensen 2002; Dankers and Leipertz 2004). This variance is much less than that of the agglomerates as measured by mobility methods, which give values of $\sigma \sim 1.6$–2.0 (Whitefield et al. 2005).

Figure 6 shows the range of $d_p$ values for a number of combustion experiments at various temperatures, including engines and flames from six references (Lee et al. 2002; Hu et al. 2003; Park et al. 2003; Dankers and Leipertz 2004; Hu and Koylu 2004; Neer and Koylu 2006). As shown in the figure, the mean values range from 27 to 30 nm with an average distribution spread ranging from ±12% to 15%. More recently, more than 5,000,000 laser-induced incandescence (LII) measurements of roadside soot (Smallwood et al. 2011) give an average value of $d_p \approx 30$–40 nm. They caution that LII measures an effective primary particle diameter, which is larger than the primary particle diameter determined by TEM imaging.

Recent scanning electron microscope (SEM) measurements of collected soot for different engine operating conditions ranging from steady-state low to high torque and transient cycle conditions on a C9 Caterpillar engine have been obtained by R. Graze (October 2009, personal communication). These measurements give a number of mean values ranging from 25 to 29 nm for the three different engine operating conditions with a standard deviation of ±20% for all conditions. Although the above-referenced measurements represent a sample of the extensive literature, they are consistent with the theory of Kazakov and Frenklach (1998). Combined with near constant values of $f(m)/\rho_p$ for soot, this gives near constant values for the property constant, $S_p$.

Another argument for an effectively constant value of $S_p$ can be based on measurements (Hong and Winter 2006) that show the refractive index function, $f(m)$, decreases with increasing primary particle size. Real-time nanoparticle growth and scattering measurements for hydrocarbon particles in plasma demonstrate that the imaginary component of the complex refractive index decreases with increasing particle size. While this plasma synthesis work has focused on interstellar dust studies, it is known that flame synthesis mechanisms for manufacturing nanoparticles are comparable to plasma synthesis.

On the basis of literature values, a fixed value of $d_p = 35$ nm has been chosen, which is the mass-weighted mean of the number mean (≈30 nm from all references) distribution occurring in the latter stages of flames and engines. This assumption is accurate within ±15%, based on the range of experimental and theoretical measurements for various combustion systems described earlier.

3.3. Surface Condensation

The mixing of primary elemental carbon (EC) soots with lower-temperature ambient air promotes heterogeneous
deposition of hydrocarbons on the surfaces of the soot agglomerate primary particles. For optical absorption methods, these coatings are in general transparent and thus are not measured. For scattering measurements, the computed value of \( f(m)/\rho_p \) for semitransparent soot compounds \((m = 1.6 – 0.01i)\) is approximately 60%–70% of that for black carbon. Given that these compounds form a surface layer on the EC primary particles, it is possible to estimate these effects on \( S_p \) by using effective medium theory (Choy 1999) combined with mass-weighted homogeneous mixing of the two components (Gangl et al. 2008). For primary particles smaller than 60 nm, Gangl et al. (2008) show that these simple approximations are in agreement with more detailed nonhomogeneous numerical calculations. Calculating the variation in \( S_p \) due to decreasing density and refractive index, with increasing primary particle diameter, results show less than 15% decrease in \( S_p \) for mass fractions of organic coatings equal to the black carbon primary particles. Thus, for engine exhaust measurements, the STAR approach has the capability to measure (within reasonable uncertainty) the total coated agglomerate mass.

### 3.4. Instrument Properties

The second term in the brackets of Equation (33) refers to the scattering measurement, \( P_{P1} \), and measured instrument parameters, \([\lambda/(P_1/\Omega)]\). The laser wavelength is well defined, and the other three parameters, i.e., laser power, sample volume path length, and receiver aperture, along with the implicit detector gain embedded in \( P_{P1} \) are all accurately determined by measuring the Rayleigh scattering from air or propane (Sorensen 2001) and described in further details in Holve et al. (2011).

### 3.5. Total Accuracy and Precision Estimates

Table 1 summarizes the standard instrument parameters, and accuracy and precision uncertainty estimates for \( C_m \). The largest contributors to absolute accuracy are the uncertainties in the soot property parameters within \( S_p = \{[\rho_p/f(m)]/(d_p/\lambda)^3 - B_f] \} \), along with the uncertainty of the \( C_m \) dependence on fractal dimension. Although individual parameter values of \( S_p \) may have greater variance, this analysis has shown that the overall product most likely has less variation. Experimental measurement uncertainties add only 1% to the overall accuracy uncertainty. The primary experimental uncertainty in the \( C_m \) propagates through the measurement of scattering ratio \( R \) and ranges from 5% for large particles to 9% at \( R = 0.85 \), corresponding to the minimum feasible agglomerate size \((\approx 75 \text{ nm})\) for this analysis.

In addition to primary particle properties, there are uncertainties in the fractal dimension, \( D_f \) which propagate through both \( S_p \) and the \( C_m \), giving a % error in the measured mass concentration \( \Delta C_m = [(2\pi d_p/\lambda)\sin(\theta/2)] \pm \Delta D_f \approx \pm 12\% \) for \( \pm \Delta D_f = 0.1 \). The estimate for overall accuracy uncertainty of \( S_p \) is based on compensating levels of uncertainty for \( d_p \) (12–15%) and \( f(m)/\rho_p \) (12–15%), as described by Hong and Winter, 2006.

![TABLE 1](https://example.com/table1)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Instrument values</th>
<th>Accuracy</th>
<th>Precision</th>
</tr>
</thead>
<tbody>
<tr>
<td>( P_1 )</td>
<td>Watts</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>( P_{P1} )</td>
<td>Watts</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>( R )</td>
<td>0</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>( S_p ) = ([\rho_p/f(m)]/(d_p/\lambda)^3 - B_f] )</td>
<td>gm/cm(^3)</td>
<td>17</td>
<td>0</td>
</tr>
<tr>
<td>( \phi )</td>
<td>Radians</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>( \Omega )</td>
<td>0.102 sr</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>( \lambda )</td>
<td>635 nm</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( I )</td>
<td>0.80 cm</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>( C_m )</td>
<td>–</td>
<td>12</td>
<td>5</td>
</tr>
<tr>
<td>STAR</td>
<td>Total ( C_m ) uncertainty</td>
<td>±21</td>
<td>±6</td>
</tr>
</tbody>
</table>

The accuracy of the gyration diameter, \( d_{go} \), measurement is similar to that of the \( C_m \), with the uncertainty varying from 5% at large particles \((< 400 \text{ nm})\) and increasing to 12% at 75 nm. The underlying accuracy of the theory is primarily based on the structure function, which is estimated to be on the order of 10%. Thus the overall uncertainty of the size measurement is \( \pm 10–15\% \), increasing for smaller particles. Similar levels of uncertainty for Differential Mobility methods are shown for comparison in the table.

### 3.6. Calculation of Primary Particle Number, Agglomerate Number, and Surface Area from \( C_m \)

It has been conjectured by many that the particle number or possibly surface area is as important or more so than the total particle mass in correlating health effects (e.g., Barone et al. 2006). It is assumed that the reduced surface area due to “necking” contact is negligible, and the majority of each primary particle is exposed to the environment. Kazakov and Frenklach (1998) make this assumption in their calculations supported by Rosner and Tandon (1994), who show that diffusion limitations on the aggregate are negligible. It is proposed to count the total number and surface area of primary particles in the agglomerates when totaling the particle number. In contrast, mobility measurements count agglomerates as one particle and thus underestimate the contribution of the much smaller primary particles (typically >50 per aggregate) tied up in the agglomerates.
Calculating the total number of primary particles and agglomerates is straightforward, namely,

\[ N_{pt} = \frac{C_m}{m_p} = \frac{6C_m}{(\pi \rho_p d_p^3)}. \]  

[34]

The total number of agglomerates is given by the total number of primary particles divided by the mean agglomerate size:

\[ N_{at} = \frac{N_{pt}}{n_{go}} = \frac{N_{pt}}{[k_o(d_{go}/d_p)^{Df}].} \]

[35]

The total particle surface area for aggregates is given by

\[ A_{pt} = \frac{N_{pt} \pi d_p^2}{6C_m/(\rho_p d_p)}. \]  

[36]

The surface area per unit mass, based on fractal agglomerates (Equation (36)), gives a factor of 2–3 higher surface area for fractal aggregates, compared with equivalent mass solid particles. Using a typical soot agglomerate number distribution (Whitefield et al. 2005), one can calculate that 85% of the surface area is composed of particles larger than the primary particle size of 35 nm. Therefore, the agglomerate surface area computed on the basis of Equation (36) from the STAR mass concentration measurement will account for more than 85% of the total soot surface area, and thus, the total agglomerate mass is a major contributor to the assessment of number and surface area through the fractal structure of soot.

4. SUMMARY

The analysis performed here differs from previous work, primarily in combining the product of primary particle number with the traditional structure factor, \( S(q) \), to obtain an expression for a “mass concentration structure factor,” denoted as the \( C_m# \). The advantage of this approach is that the \( C_m# \) and gyration diameter, \( d_g \), are dependent only on the scattering ratio at two angles, for a specified fractal dimension \( D_f \). For polydisperse soot agglomerate distributions, the \( C_m# \) formulation provides lower-order scattering moments that are less sensitive to variations in the size distribution. This leads to simple relationships for computing the mass concentration and agglomerate gyration diameter in terms of two scattering signals at known scattering angles and optical geometry. These results assume only that the soot parameter for primary particles expressed as \( S_p = \rho_p/[d_p/\lambda^{3-D_f} f(m)] \), and the fractal dimension, \( D_f \), of the soot agglomerate are near constant, a result that is suggested by a range of studies on combustion flames and engines.

Table 1 provides a framework to test the validity of the STAR method and assumptions with additional experimental measurements. PFA theory shows that one does not need to assume an average value of density for soot agglomerates, frequently used for converting mobility measurements to total mass. There is sufficient evidence now to use PFA theory to define the density distributions for soot aggregates. The present analysis using the results of Nicolai et al. (1994) suggests that experimental results giving \( k_o = 2 \) are consistent with generally assumed density correlation functions that assume \( y = 2 \) and \( d_p^∗ = \) the measured monomer size \( d_p \). Recent measurements by Hu and Koylu (2004) appear to be converging on a value of \( k_o = 2 \pm 20\% \).

Evaluation of the refractive index for combustion soots combined with density would lead to more accurate measurements, but the apparent uncertainty for scattering measurements is less than previously assumed uncertainty because all soot properties are embedded as one product defined as the soot property parameter, \( S_p \). Although the primary particle diameter, \( d_p \), must be assumed for low concentration applications in which measurement by extinction combined with scattering methods are infeasible, there are many results showing that the variance of \( d_p \) is small (±15%), and some of this variance may be compensated by the variance in \( f(m)/\rho_p \). The fractal dimension appears to be quite stable for a wide variety of combustion systems and fuels with a mean value of 1.8 (±6%). The aggregate particle size distribution widths are also well known, and at the same time, any variations in the particle distribution width tend to cancel out because they appear as a ratio of the distribution moment functions. Indeed, if \( q \) is maximized, the instrument will operate in the “large agglomerate” limit, where the agglomerate size distribution moment function ratio reduces to unity. The concentration measurement then becomes independent of the agglomerate size and distribution, illustrating the wisdom of Sorensen’s (2001) maxim of focusing on \( q \) as the important scattering parameter.

The sensitivity analysis has shown that the absolute value of scattering using literature values of the refractive index is probably within ±21% of the true value, while the precision is ±6%. Park et al. (2003b) and Symonds et al. (2007) have performed detailed measurement comparisons of filter and other mobility methods, obtaining comparisons with a similar level of uncertainty, namely, ±18%–20%. Determination of a more accurate value requires detailed mass comparisons with conventional mass measurements, although one needs to be mindful of the intrinsic precision in gravimetric measurements, which at high concentrations, are typically on the order of ±10% for repeat measurements. As described in Holve et al. (2011), this level of accuracy or precision for gravimetric measurements is not attainable for current engine emission measurements following a diesel particulate filter and dilution, whereas equivalent optical scattering measurements by STAR show little change in accuracy or precision.

REFERENCES


